1-N7-51 / 1 / 1

Closure of the Oak Ridge National Laboratory Hydrofracture Facility: An Opportunity to Study the Fate of Radioactive Wastes Disposed of by Subsurface Injection I

C. Stephen Haase

CONF-8709170--1

Karen L. Von Damm

DE88 001738

Stephen H. Stow

Environmental Sciences Division

Oak Ridge National Laboratory

Oak Ridge, Tennessee 37831-6317

ABSTRACT

At Oak Ridge National Laboratory, subsurface injection has been used to dispose of liquid low-level nuclear waste for the past two decades. The process consists of mixing the liquid waste with cement and other additives to form a slurry that is injected under pressure through a cased well into a low-permeability shale at a depth of approximately 300 m (1000 ft). The slurry spreads from the well along hydraulic fractures and sets to form irregularly shaped grout sheets of up to 200 m (650 ft) in radius.

Over 2.6 x 106 gal (1.8 x 107 L) of slurry, containing more than 5.5 x 1016 Bq (1.5 x 106 Ci) of radionuclides (principally 90Sr and 13/Cs), have been disposed of since this process was developed in

"The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. DE-AC05-840R21400. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government

MASTER DESCRIPTION OF THE PERSON OF THE PERS

. Bec.

Research sponsored by Office of Defense Waste and Transportation Management, U.S. Department of Energy, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

'the early 1960s. Under its underground injection control regulations, the state of Tennessee has tentatively assigned a Class V status to the well.

In 1986, the U. S. Department of Energy, owner of the facility, decided to close the site. Closure-related site characterization provides a unique opportunity to study the fate of the injected wastes. A series of monitoring wells are in place to measure groundwater chemistries within the injection strata and within overlying and underlying confining units. Initial results indicate that (1) contaminated groundwater surrounds the grout sheets in the injection zone, extending at least as far as 300 m (1000 ft) from the injection well; (2) contaminated groundwater is largely and perhaps exclusively confined to the host formation; and (3) of the two principal radionuclides disposed of (90Sr and 137Cs), only 90Sr is present in the contaminated groundwater. The illite-rich mineralogy of the the injection formation strongly absorbs 137Cs and greatly retards its migration. Movement of 90Sr, however, is not as greatly retarded by the injection formation. Geochemical modeling is being used to identify and to evaluate hydrogeological controls on 90Sr behavior. Preliminary results suggest that the ground waters within the injection formation are saturated with Sr from natural sources, and that 90Sr mobility may be lessened by precipitation/dissolution reactions associated with such a saturated condition.

INTRODUCTION

During the past two decades, Oak Ridge National Laboratory (ORNL) has disposed of over 5.6 x 10¹⁶ Bq (1.5 x 10⁶ Ci) of liquid low-level radioactive waste by subsurface injection using the hydrofracture process. In this process, liquid radioactive wastes are mixed with solids to form a cementitious slurry that is pumped underground through a cased injection well. The slurry spreads out into hydraulically fractured intervals in a low-permeability host rock through slots at the bottom of the injection well casing (Fig. 1). It forms irregularly shaped, pancake-like sheets and solidifies into a grout that encapsulates the wastes. The principal radionuclides disposed of are ⁹⁰Sr and ¹³⁷Cs, although others, including ³H, ⁶⁰Co, ¹⁰⁶Ru, and isotopes of Cm, U, Am, and Pu, also occur in the wastes.

The hydrofracture process has been developed at ORNL over the last quarter of a century (deLaguna 1968; IAEA 1983). Initial development work was performed at three test facilities. In the mid-sixties, the process became operational, and approximately 2.8 x 10¹⁶ Bq (7.5 x 10⁵ Ci) of radioactive wastes were disposed of at the modified third test facility from 1965 through 1979. A fourth injection facility, located approximately 240 m (800 ft) from the third facility, was put into operation in 1982. Over 2.8 x 10¹⁶ Bq (7.5 x 10⁵ Ci) of radionuclides have been disposed of since 1982 (Weeren, McDaniel, and Lasher 1985). Because significant amounts of radionuclides were injected only at the third and fourth sites, and because they are located close together, they will be considered as the "ORNL hydrofracture site" for the remainder of this paper. The first two experimental sites will not be considered further.

The purpose of this paper is to discuss available information on the fate of radionuclides injected at the ORNL hydrofracture site. A brief summary of the hydrofracture subsurface injection process and its operational history is presented. A summary of the current regulatory status and of site hydrogeology is also included as background for subsequent sections of the paper. Data are presented on the chemical compositions of the groundwaters from monitoring wells finished within the injection and confining zones at the facility. Finally, preliminary results from geochemical modeling of the groundwater within the injection zone are presented, and the role of modeling in understanding the fate of injected radionuclides is discussed.

THE HYDROFRACTURE PROCESS

Details of the ORNL process and a summary of operations at the new hydrofracture facility through 1984 have been presented previously (Weeren, McDaniel, and Lasher 1985; Haase, Zucker, and Stow 1985; Stow et al. 1985; Stow and Haase 1986; Haase and Stow 1987). The hydrofracture process is a large-scale batch process that makes use of standard operating and engineering practices from hydraulic fracturing technology as applied in the petroleum industry (Fig. 1). Liquid radioactive wastes were

stored in underground storage tanks and disposed of typically every 1 to 2 years. The waste solutions, which were alkaline and nitrate-rich (1 to 2 M NaNO3), were blended with cement and othe; additives to form a slurry, which was pumped under approximately 20- to 25-MPa (2800- to 3500-psi) pressure into a cased injection well. The casing was slotted at a depth of approximately 300 m (1000 ft). Hydraulic fractures in the host rock, a shale of low porosity and permeability, were initiated along bedding planes by pumping several thousand liters of water into the well; this was followed immediately by the waste-bearing slurry, which spread radially from the injection well along the hydraulic fractures. The slurry sets to form thin (less than a few centimeters) grout sheets that extend up to several hundred meters from the well. No grout sheets have been detected more than 210 m (700 ft) from the injection point. Later injections were made through slots cut at shallower depths in the well, thus allowing maximum use of the host injection strata. The shallowest injection depths used at the ORNL hydrofracture facility were approximately 230 m (750 ft). Disposal was normally done over a 2-d period in two 8- to 10-hour shifts. The total volume of radioactive-waste-bearing slurry disposed of in a single injection was typically 760,000 to 940,000 L (200,000 to 250,000 gal).

OPERATIONAL HISTORY OF THE ORNL HYDROFRACTURE FACILITIES

Experimental hydrofracture injections at the third facility began in 1963, and operational injections began in 1965 (deLaguna et al. 1968). Seven experimental and eighteen operational injections were completed during the period 1963 to 1979. Operational details for these injections are summarized in deLaguna et al. 1968; Weeren 1974; Weeren 1976; and Weeren 1980. The major radionuclide inventory injected during this period was ⁹⁰Sr [1.42 x 10¹⁵ Bq (38,600 Ci)] and ¹³⁷Cs [2.23 x 10¹⁶ Bq (604,000 Ci)]. Total volume of the grout slurry disposed of at any one injection ranged from 150,000 to 870,000 L (40,000 to 230,000 gal), and the total amount of waste-bearing grout injected during the 25 injections was 8,800,000 L (2,200,000 gal).

Construction of the new hydrofracture facility began in November 1979 and was completed in February 1982. A preoperational test was conducted in March 1982, and the facility became operational in June 1982. During the life span of the new facility, thirteen injections were made, with the last injection being completed in January 1984 (Weeren, McDaniel, and Lasher 1985). In contrast with operations at the third hydrofracture facility, where injections were made on an 18- to 24-month period, injections at the fourth facility were made typically on a 4- to 6-week basis. The major radionuclide content totals for the 13 injections were: 90 Sr [2.39 x 1016 Bq (645,000 Ci)] and 137 Cs [3.06 x 1015 Bq (82,800 Ci)]. Additional data on individual injections are presented elsewhere (Weeren 1984; Weeren, McDaniel, and Lasher 1985). Total volumes of grout slurry disposed of at any one injection ranged from 580,000 to 1,190,000 L (150,000 to 314,000 gal), and the total amount of waste-bearing grout slurry injected during the 13 injections was 10,874,000 L (2,900,000 gal).

REGULATORY CLASSIFICATION AND STATUS

Both federal and Tennessee underground injection control (U!C) regulations define five classes of injection wells that cover the most frequently used underground injection waste disposal processes. Because of its unique design and application to radioactive waste disposal, the ORNL hydrofracture facility does not fall unambiguously into any one of the five UIC well classes (Stow and Haase 1986; Haase and Stow 1987). The state has tentatively agreed to assign the injection well at the new facility a Class V status; Class V is a "catch-all" category for, among other things, injection wells that employ new and innovative technologies. The U. S. Environmental Protection Agency has not yet established a position on well classification and has raised the question of the possible existence of an underground source of drinking water (USDW) below the injection zone. If a USDW exists under the site, then the injection well is automatically placed into Class IV; Class IV wells require immediate shutdown - a moot point for the ORNL site, because the facility is presently closed. The need to classify the injection well as IV or V may eventually necessitate construction of a 1,500-m- (5000-ft-) deep exploratory well through strata underneath the ORNL site to determine if a USDW exists. A Class I status (for hazardous

wastes) cannot be assigned because the injection pressures were, of course, great enough to cause fracturing of the host injection strata.

In early 1986, the United States Department of Energy (DOE) decided not to file for an injection permit for the new hydrofracture facility (Haase and Stow 1987). Guidance received from the federal and state regulators specified that a site closure plan should be prepared if a permit for the injection well was not to be requested. At the present time, all hydrofracture sites are being closed under both UIC regulations and the provisions of the Resource Conservatrion and Recovery Act.

SITE GEOLOGY

The ORNL hydraulic fracturing facility is within DOE's Oak Ridge Reservation in east Tennessee (Fig. 2). The site is located in the Valley and Ridge province of the Appalachian Mountains, which in east Tennessee is characterized by a series of Alleghenian (250 my old) regional thrust faults that strike parallel to the borders of the province and extend from Alabama to Virginia. Motion along these thrust faults resulted in the formation of a series of imbricate thrust sheets that repeat a stratigraphic succession consisting of sandstones, shales, and limestones as many as seven times from the southeastern to the northwestern border of the province.

The ORNL hydrofracture site occurs on the leading edge of the Copper Creek thrust sheet, within 1 km (3200 ft) of where the fault comes to the surface (Fig. 3). The strike of strata at the site is N 45° to 55° E, and the dip of the strata is variable with subsurface values typically ranging from 10° to 20° to the southeast.

The injection formation for the ORNL hydrofracture facility is the Pumpkin Valley Shale. This formation is the basal unit of the Conasauga Group, which consists of alternating clastic-rich and

ORNL site and consists of interbedded shales, mudstones, and shaly siltstones (Haase 1983; Haase, Walls, and Farmer 1985; Haase, Zucker, and Stow 1985). The upper confining zone consists of the Rutledge Limestone and the Rogersville Shale, which are the two formations immediately overlying the Pumpkin Valley Shale. Together, these formations are approximately 70 m (230 ft) thick at the ORNL site. The Rutledge Limestone is a shale-rich carbonate with only a few relatively pure limestone horizons that average 1 to 3 m (3 to 10 ft) in thickness each. The overlying Rogersville Shale consists of mudstones and shales with locally abundant siltstone stringers (Haase, Walls, and Farmer 1985; Dreier et al. 1987). The lower confining unit is the Rome Formation. This formation is approximately 110 m (360 ft) thick at the ORNL site. The uppermost Rome Formation is a massive, fine-grained sandstone approximately 15 m (50 ft) thick. The remainder of the formation consists of interbedded sandstone, siltstone, and shale horizons that range in thickness from 2 to 20 m (6 to 65 ft) each. All strata of the injection zone and the confining units contain multiple joint sets and several generations of small-scale folds and faults (Sledz and Huff 1981; Haase, Walls, and Farmer 1985; Haase, Zucker; and Stow 1985; and Dreier et al. 1987) that are associated with Alleghenian thrust faulting. More detailed discussions of the site geology for the ORNL hydrofracture facility are presented in Haase (1983); Haase, Zucker, and Stow (1985); Haase (1987); and Dreier et al. (1987).

SITE HYDROLOGY

The hydrology of the ORNL hydrofracture site is complex. Available data suggest that the subsurface groundwater regime consists of a shallow, freshwater system and a deep saline system (Haase, Zucker, and Stow 1985). In general, the permeability of the Conasauga Group is low, and flow directions for much of the shallow groundwater system are influenced by the structural fabric, such as joints and fractures (Sledz and Huff 1981; Rothschild, Haase, and Huff 1984; Smith and Vaughan 1985; Dreier and Solomon 1987). The shallow groundwater system at the site extends to depths of 60 to 150 m (200 to 500 ft). Groundwater within this system is fresh, with total dissolved solids (TDS) values \leq 5000 μ g/mL. Within the upper portions of the zone of shallow fresh groundwater, at depths \leq 50 m (\leq 150 ft),

the weathered portions of Conasauga Group strata contain large amounts of groundwater. Below this depth, borehole geophysical logs (Haase 1987) suggest that fresh groundwater is increasingly confined to fractures and fault zones.

Waters within the deep saline groundwater system are high-TDS fluids (see Table I) with Cl-concentrations ranging from 75,000 to 150,000 µg/mL (Switek, Haase, and Stow 1987; Haase, Switek, and Stow 1987). The lower-ionic-strength waters that occur in the deep groundwater system cannot be classified into a single category based on predominant anion and cation analyses, although Cl-Na-Ca (on a molar basis) is the most common. Sodium is always the most abundant cation, followed by calcium and then magnesium in every case. For the anions, Cl- or HCO₃- is the most abundant, followed by a varying order in the other anions, including SO₄-2, F-, and Br. These relationships show that the fluids have complex histories and interrelationships.

Because of the dramatic compositional differences between shallow and deep groundwaters, the deep system is thought to be largely isolated from the shallow system. Details of possible coupling between the two systems are not known. By analogy with the shallow groundwater system, it is hypothesized that flow directions of the deep system are largely controlled by the fracture permeability related to the structural fabric. Laboratory measurements from drill core samples of the Pumpkin Valley Shale indicate exceedingly low permeability values in the range of 0.3×10^{-9} to 0.03×10^{-9} darcy, and porosity values range from ≤ 1.0 to 3.0% (deLaguna et al. 1968).

FATE OF INJECTED WASTES

Contaminated groundwater was discovered in August 1984 in two groundwater monitoring wells drilled to investigate hydrological conditions in the host formation (Haase, Switek, and Stow 1987). Three

monitoring wells, DM1, DM2, and DM3a² (Fig. 4), were drilled at distances of 300 m (1000 ft) from the injection well. Two of the wells, DM1 and DM2, are along geological strike to the east and west, respectively, from the injection well. The third well, DM3a, is updip to the northwest of the injection well. Contamination was observed in wells DM1 and DM2, while groundwater in well DM3a is uncontaminated. The principal radionuclide contaminant is ⁹⁰Sr, with concentrations ranging from 70,000 to 150,000 Bq/L (1.90 to 4.0 μCi/L; Haase, Switek, and Stow 1987). Only trace amounts of several other radionuclides known to have been disposed of at the new facility (³H and ¹⁰⁶Ru) have been noted. Although large quantities of ¹³⁷Cs were disposed of, this radionuclide has not been observed in the groundwaters.

The discovery of significantly contaminated groundwater in the injection formation was not anticipated because the cementitious grout was designed to incorporate the radionuclide-bearing wastes (Stow and Haase 1986). Although the concentration of ⁹⁰Sr observed in the contaminated groundwaters is approximately 0.01% of the concentration of this radionuclide in the slurries originally injected [average ⁹⁰Sr concentrations in the injected slurries were approximately 2.0 x 10⁹ Bq/L (54 mCi/L)], the levels are high enough to be of concern.

The discovery of groundwater contamination in the injection formation was a contributing factor in the decision to close the hydrofracture facility (Haase and Stow 1987). Furthermore, evaluation of the groundwater contamination is a central issue in the remedial investigation process being undertaken as

These wells were originally designated as DM1, DM2, and DM3a and initially were completed with a large [approximately 274 m (900 ft)] open interval to facilitate hydrological testing in both the injection and confining zones. During subsequent modification, DM1 and DM2 were reconfigured to monitor the lower confining unit (Rome Formation), and were renamed DM1-RM and DM2-RM. Well DM3a was reconfigured to monitor only the injection formation (Pumpkin Valley Shale), and was renamed DM3a-PV (see Table 1 and Fig. 4).

the first step in the closure process. Four major issues are to be addressed in the investigation of the contaminated groundwater: (1) determination of the extent and magnitude of the groundwater contamination, (2) determination of groundwater quality within the injection zone and the upper and lower confining units, (3) determination of the hydrological flow regime within the injection formation and confining units, and (4) determination of the fate of the radionuclide contaminants in the groundwater.

This paper principally addresses issue (4), especially as it pertains to the two major radionuclides, ⁹⁰Sr and ¹³⁷Cs, injected at the ORNL facility. A twofold approach, involving direct observation and geochemical modeling, is being followed to address the "fate" issue. Data from the monitoring wells installed around the ORNL hydrofracture facility provide a unique opportunity to directly examine groundwater chemistry within the injection formation and the confining units. Geochemical modeling of the groundwater chemistry can then be used to identify key geochemical parameters and mechanisms controlling the migration and fate of the injected radionuclides.

GROUNDWATER MONITORING RESULTS

Subsequent to the discovery of contamination, the initial three DM wells were reconfigured to allow investigation of specific subsurface intervals, and additional wells were installed near the hydrofracture facility (Table 1). In addition to the reconfigured and new DM wells, other wells penetrating the injection zone near the hydrofracture facility were sampled (Table 1). Detailed discussion of groundwater monitoring results from these wells are presented in Haase, Switek, and Stow (1987) and Switek, Haase, and Stow (1987). The following is a brief summary of the results presented in these reports.

Injection Formation

Groundwater chemical data from the injection formation indicate that contamination occurs in wells DM1-PV and DM2-PV³ only. Wells DM3a-PV and WOL No.1, as well as the four-well cluster at the second hydrofracture site (see Table 1 and Fig. 4) are uncontaminated. Thus, groundwater contamination extends to distances greater than 300 m (1000 ft), but less than 900 m (3,000) to the east and 1200 m (4000 ft) to the west of the ORNL injection hydrofracture facility. Groundwater contamination is also absent in the only updip well available for sampling at this time, DM3a-PV. Water quality is spatially variable throughout the injection zone (see analyses 1 and 4 in Table 2). Available data also indicate that the levels of contaminants within the two contaminated wells vary with time (see analyses 1 through 3 in Table 2).

Confining Units

Some groundwater quality data for wells finished in the upper and lower confining units (see Table 1) are also presented in Table 2. Data for the upper confining unit indicate only very slight levels of ⁹⁰Sr contamination in groundwater from wells adjacent to the injection well [within 120 m (400 ft)] at the fourth facility (Switek, Haase, and Stow 1987) (see analysis 5 in Table 2). Groundwaters from the upper confining unit sampled in wells DM1-RT and DM3-RT located 300 m (1000 ft) from the injection well at the fourth hydrofracture facility also contain slight amounts of contamination (Haase, Switek, and Stow 1987) (see analysis 6 in Table 2). Available data for wells DM1-RM and DM2-RM in the lower confining unit suggest the possibility of contamination in at least the upper part of this horizon (Haase, Switek, and Stow 1987) (see analysis 7 in Table 2). These wells were two of the initial DM wells and

These two new wells were drilled to replace the initial DM wells in which contamination was first discovered. As noted previously, the initial DM wells (DM1 and DM2) were reconfigured to monitor the Rome Formation and were renamed DM1-RM and DM2-RM.

had standing columns of contaminated water in them for approximately 1 year prior to being reconfigured. Because of this, much of the contamination may be due to infiltration of contaminated fluid from the borehole during the period prior to the reconfiguration and may not represent actual groundwater contamination within the lower confining layer (Haase, Switek, and Stow 1987).

Additional sampling and well development activities are in progress in an attempt to resolve uncertainties concerning the presence or absence of groundwater contamination in the lower confining unit.

Discussion of Groundwater Monitoring Results

Of the two principal radionuclides disposed of, ⁹⁰Sr occurs in significant concentrations in contaminated groundwaters, while ¹³⁷Cs has not been detected. Such results can be explained, at least in part, by consideration of the cation exchange and adsorption properties of the host formation (Haase, Zucker, and Stow 1985). The clay mineralogy of the Pumpkin Valley Shale is relatively simple, with illite and illite/vermiculite accounting for as much as 80% of the clay content of the formation. Because these clay minerals have high sorption properties for ¹³⁷Cs, the Pumpkin Valley Shale is extremely efficient in sorbing and retaining this radionuclide (deLaguna et al. 1968). Available data indicate, however, that the mineralogical composition of the Pumpkin Valley Shale is much less favorable for sorption and retention of ⁹⁰Sr (deLaguna et al. 1968). Under ambient geochemical conditions, the illite and illite/vermiculite in the Pumpkin Valley Shale are inefficient in retaining ⁹⁰Sr, and no other mineralogical constituent of the formation is an effective sorption agent for this radionuclide. Thus, mobility of any ⁹⁰Sr not incorporated by the grout itself would be little affected by properties of the host formation.

GEOCHEMICAL MODELING

In order to elucidate the geochemical controls on the compositions of the groundwaters at the hydrofracture site, modeling of their compositions using the geochemical modeling code EQ3NR/EQ6 (Wolery 1983) in conjunction with analytical data obtained from repeated samplings of the hydrofracture

wells (Haase, Switek, and Stow 1987; Switek, Haase and Stow 1987) has been initiated. The computer code EQ3NR allows the speciation of water constituents and the saturation index of several hundred minerals to be calculated, which in turn permits an evaluation of whether the groundwaters are in equilibrium with the enclosing rock formation. The EQ6 computer code is a reaction path program that permits calculations related to mixing of groundwaters, reaction of groundwaters with various rocks and/or minerals, and inclusion of kinetics and other parameters to determine "what if" scenarios regarding the groundwaters and rocks. Results from EQ3NR/EQ6 are limited by the availability and quality of relevant thermodynamic data and the constraints of an equilibrium model. Many of the hydrofracture groundwaters, with their extremely high ionic strengths and brine compositions, present an additional difficulty and must be modeled using Pitzer (1973) or Harvie, Møller, and Weare (1984) coefficients and equations, in contrast to the Debye-Huckel equation which is utilized in most speciation codes.

All three of these options are available in the latest version of EQ3NR/EQ6. The strategy has been to (1) examine the groundwaters for mineral saturations and speciation, (2) examine the groundwater-host rock system to see if it is in equilibrium, (3) study the effects of mixing between various hydrofracture-related solutions and other groundwater compositions, and (4) study the reaction of groundwaters of different compositions with various rock lithologies.

Modeling of low-ionic-strength (<1) hydrofracture groundwaters, which are primarily from the Pumpkin Valley Formation sampled by well DM3a-PV, has begun. Because redox data are unavailable each groundwater composition was modeled twice, first assuming that the solutions are in equilibrium with air and second assuming that the concentration of HS- in the waters is 0.001 of the measured SO₄-2 concentrations. No H₂S odor was detected in these solutions at the time of sampling, and this assumption gives HS- concentrations in line with this observation. Also a ratio similar to this has been observed in other shale groundwaters (Von Damm 1987). These calculations provide two limiting cases, one very oxidizing and one very reducing. The calculations suggest that the waters are saturated

or supersaturated with respect to several carbonate minerals (calcite, dolomite, strontianite, smithsonite). sulfate minerals (barite, celestite), aluminosilicates (albite, k-feldspar, illite, kaolinite, several iron chlorites, and various other clay minerals), several silica phases (quartz, tridymite, cristobalite), and, in addition for the reducing case, several sulfides (pyrite, sphalerite, wurtzite). Not all groundwaters are saturated or supersaturated with all of these phases; groundwaters with pH values <7.5 are undersaturated with respect to carbonates. Because the groundwaters are found to be saturated or supersaturated with respect to both a strontium carbonate (strontianite) and strontium sulfate (celestite), the geochemical controls on the mobility of strontium will not be strictly a function of the pH of the solutions. In general, the mineral assemblages with which the groundwaters are calculated to be saturated or supersaturated are in excellent agreement with the mineral assemblages observed in the Pumpkin Valley Shale (Haase 1983), an observation that suggests that the groundwaters are in equilibrium with the enclosing rock formation. Modeling of the higher-ionic-strength solutions is just beginning. Preliminary results suggest that these groundwaters are also saturated with celestite and strontianite, and in addition, halite (NaCl). Modeling of the hydrofracture brines and reaction path modeling are the next steps in attempting to more fully understand the geochemical controls on the compositions of the hydrofracture groundwaters.

Fate of ⁹⁰Sr in the Injection Zone. Results obtained from geochemical modeling indicate that many of the low-and high-ionic-strength hydrofracture groundwaters are saturated or supersaturated with the minerals celestite (SrSO₄) and/or strontianite (SrCO₃). This observation suggests that the strontium concentration in the groundwaters may be controlled by equilibrium with these phases, which would have the net effect of retarding the mobility of strontium in this system.

SUMMARY

Groundwater chemistry data from monitoring wells within the injection strata and the overlying and underlying confining units at the ORNL hydrofracture site indicate that contaminated groundwater

extends at least as far as 300 m (1000 ft) from the injection well surrounding the grout sheets in the injection zone. The contaminated groundwater, however, appears to be largely confined to the injection formation. The data also indicate that, of the two principal radionuclides disposed of (90 Sr and 137 Cs), only 90 Sr is present in the contaminated groundwater. The illite-rich mineralogy of the injection formation strongly absorbs 137 Cs and greatly retards its migration. Movement of 90 Sr, however, is not as greatly retarded by the injection formation. Preliminary results from geochemical modeling suggest that the groundwaters within the injection formation are saturated with Sr from natural sources, and that 90 Sr mobility may be lessened by precipitation/dissolution reactions associated with such a saturated condition.

REFERENCES

deLaguna, W., T. Tamura, H. O. Weeren, E. G. Struxness, W. C. McClain, and R. C. Sexton 1968. Engineering development of hydraulic fracturing as a method for permanent disposal of radioactive wastes. ORNL-4259. Oak Ridge National Laboratory Report, Oak Ridge, Tennessee.

Dreier, R. B., and D. K. Solomon 1987. Fracture characterization in the unsaturated zone of a shallow land burial facility. Journal of Geophysical Research (in press).

Dreier, R. B., C. S. Haase, C. M. Beaudoin, H. L. King, J. Switek, and R. J. Selfridge 1987. Summary of geological data in the vicinity of the hydrofracture facilities. ORNL/RAP/LTR-87/26. Oak Ridge National Laboratory Report, Oak Ridge, Tennessee.

Haase, C. S. 1983. Geological and petrological considerations relevant to the disposal of radioactive wastes by hydraulic fracturing: An example at the U.S. Department of Energy's Oak Ridge National Laboratory. pp. 307-314. IN D. G. Brookins (ed.), Proceedings 6th International Symposium on the Scientific Basis for Nuclear Waste Management. Elsevier, New York.

Haase, C. S. 1987. Geophysical data from boreholes DM1, DM2, DM3, and DM3a, Oak Ridge National Laboratory, Oak Ridge, Tennessee. ORNL/TM-9681. Oak Ridge National Laboratory Report, Oak Ridge, Tennessee.

Haase, C. S., E. C. Walls, and C. D. Farmer 1985. Stratigraphic data for the Conasauga Group and the Rome Formation on the Copper Creek fault block near Oak Ridge, Tennessee: preliminary results from test borehole ORNL-JOY No. 2. ORNL/TM-9159. Oak Ridge National Laboratory Report, Oak Ridge, Tennessee

Haase, C. S., C. L. Zucker, and S. H. Stow 1985. Geology of the host formation for the New Hydraulic Fracturing Facility at Oak Ridge National Laboratory. pp. 473-480. IN R. G. Post and M. E. Wacks (eds.), Proceedings of Waste Management '85. Volume 2. University of Arizona Press, Tucson, Arizona.

Haase, C. S., and S. H. Stow 1987. Status of the Oak Ridge National Laboratory New Hydrofracture Facility: implications for the disposal of liquid low-level radioactive wastes by underground injection. pp. 227-233. IN R. G. Post and M. E. Wacks (eds.), Proceedings of Waste Management '87. Volume 3. University of Arizona Press, Tucson, Arizona.

Haase, C. S., J. Switek, and S. H. Stow, 1987. Geochemistry of formation waters in the lower Conasauga Group at the New Hydrofracture Facility: Preliminary data from the Deep Monitoring (DM) wells. ORNL/RAP-6. Oak Ridge National Laboratory Report, Oak Ridge, Tennessee.

Haase, C. S., J. Switek, S. H. Stow, H. L. King, and P. H. Pollard 1987. Chemical and radionuclide data from the DM and associated wells at the Hew Hydrofracture Facility, Fall 1986. ORNL/RAP/LTR-86/95. Oak Ridge National Laboratory Report, Oak Ridge, Tennessee.

Harvie, C. E., N. Møller, and J. H. Weare 1984. The prediction of mineral solubilities in natural waters: the Na-K-Mg-Ca-H-Cl-SO₄-OH-HCO₃-CO₂-CO₂-H₂O system to high ionic strengths at 25°C. Geochimica et Cosmochimica Acta. 48:723-751.

International Atomic Energy Association (IAEA) 1983. Disposal of Radioactive Grouts in Hydraulically Fractured Shale. IAEA Technical Report Series No. 232. Vienna, Austria.

Pitzer, K. S. 1973. Thermodynamics of electrolytes I: theoretical basis and general equations. Physical Chemistry. 777:268-277.

Rothschild, E. R., C. S. Haase, and D. D. Huff 1954. Geological influence on shallow groundwater flow in the Conasauga Group near Oak Ridge, Tennessee (abstract). Geological Society of America Abstracts with Program 17:132.

Sledz, J. J., and D. D. Huff 1981. Computer model for determining fracture porosity and permeability in the Conasauga Group, Oak Ridge National Laboratory. ORNL/TM-7695. Oak Ridge National Laboratory Report, Oak Ridge, Tennessee.

Smith, E. D., and N. D. Vaughan 1985. Experiences with aquifer testing and analysis in fractured low permeability sedimentary rocks exhibiting nonradial pumping response. pp. 137-149. IN Hydrogeology of Rocks of Low Permeability. USA Members of the International Association of Hydrogeologists, Tucson, Arizona.

Stow, S. H., C. S. Haase, J. Switek, G. R. Holzhausen, and E. Majer 1985. Monitoring of surface deformation and microseismicity applied to radioactive waste disposal through hydraulic fracturing at Oak Ridge National Laboratory. pp. 481-485. IN R. G. Post and M. E. Wacks (eds.), Proceedings of Waste Management '85. Volume 2. University of Arizona Press, Tucson, Arizona.

Stow, S. H., and C. S. Haase 1986. Subsurface disposal of liquid low-level radioactive wastes at Oak Ridge, Tennessee. pp. 656-675. IN Proceedings of the International Symposium on Subsurface Injection of Liquid Wastes. National Water Well Association, Dublin, Ohio.

Switek, J., C. S. Haase, and S. H. Stow 1987. Geochemistry of formation waters in the lower Conasauga Group at the New Hydrofracture Facility: Preliminary data from the Rock Cover (RC) wells. ORNL/RAP-5. Oak Ridge National Laboratory Report, Oak Ridge, Tennessee.

Von Damm, K. L. 1987. Geochemistry of shale groundwaters: survey of available data and postulated mineralogic controls on composition. ORNL/TM-10488. Oak Ridge National Laboratory Report, Oak Ridge, Tennessee.

Weeren, H. O. 1974. Shale fracturing injections at Oak Ridge National Laboratory - 1972 series. ORNL/TM-4467. Oak Ridge National Laboratory Report, Oak Ridge, Tennessee

Weeren, H. O. 1976. Shale fracturing injections at Oak Ridge National Laboratory - 1975 series. ORNL/TM-5545. Oak Ridge National Laboratory Report, Oak Ridge, Tennessee.

Weeren, H. O. 1980. Shale fracturing injections at Oak Ridge National Laboratory - 1977 to 1979 series. ORNL/TM-7421. Oak Ridge National Laboratory Report, Oak Ridge, Tennessee.

Weeren, H. O. 1984. Hydrofracture injections at Oak Ridge National Laboratory - 1982 to 1984 series. ORNL/NFW-84/43. Oak Ridge National Laboratory Report, Oak Ridge, Tennessee.

Weeren, H. O., G. D. Brunton, W. deLaguna, and J. G. Moore 1974. Hydrofracture Site Proof Study at Oak Ridge National Laboratory. ORNL/TM-4713. Oak Ridge National Laboratory Report, Oak Ridge, Tennessee.

Weeren, H. O., E. C. McDaniel, and L. C. Lasher 1985. Status of Hydrofracture Operations at Oak Ridge National Laboratory. pp. 465-471. IN R. G. Post and M. E. Wacks (eds.), Proceedings of Waste Management '85. Volume 2. University of Arizona Press, Tucson, Arizona.

Wolery, T. J. 1983. EQ3NR computer program for geochemical aqueous speciation-solubility calculations: user's guide and documentation. UCRL-55414. Lawrence Livermore National Laboratory Report, Livermore, California.

FIGURE CAPTIONS

- Figure 1. Conceptual diagram illustrating major features of the ORNL hydrofracture process. Wastes are held prior to injection in storage tanks. Solids used to mix the slurry are held in bulk storage tanks. Slurry is mixed at wellhead and pumped underground through injection well. Observation wells are used to determine the location of injected slurries. Scale is approximate.
- Figure 2. Location map for the Oak Ridge locality. The ORNL hydrofracture facilities are located within the study area indicated.
- Figure 3. Geological cross section through the ORNL hydrofracture site. The section is oriented approximately north-south, perpendicular to the strike of the Copper Creek thrust fault. The subsurface distribution of the Rome Formation (lower confining unit), the Pumpkin Valley Shale (injection formation), and the Rogersville Shale and Rutledge Limestone interval (upper confining unit) are illustrated.
- Figure 4. Location map illustrating the fourth (new) hydrofracture facility at ORNL. Locations of the seven DM wells (Table 1) are illustrated. Rock cover wells (Table 1) are located within the hachured region surrounding the injection well (labeled INJ). Well WOL No. 1 occurs off the map to the left of well DM2-RM [approximately 1200 m (4000 ft) west of the injection weil]. Wells at the HF2 site (Table 1) are off the map to the right of well DM1-RT [approximately 900 m (3000 ft) east of the injection well].

REPRODUCED FROM BEST AVAILABLE COPY

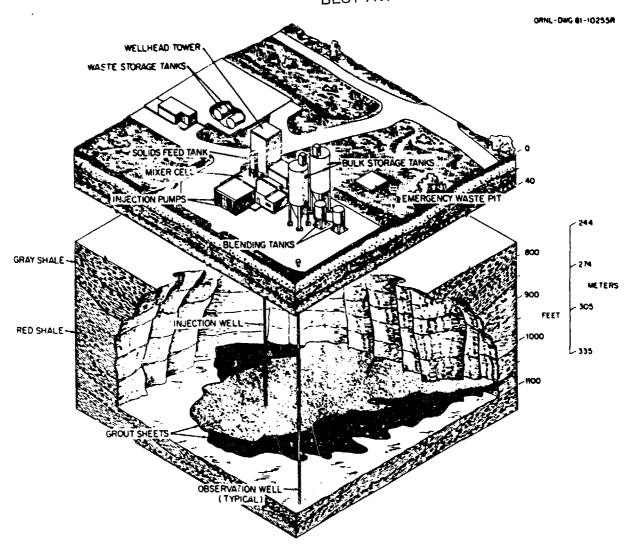
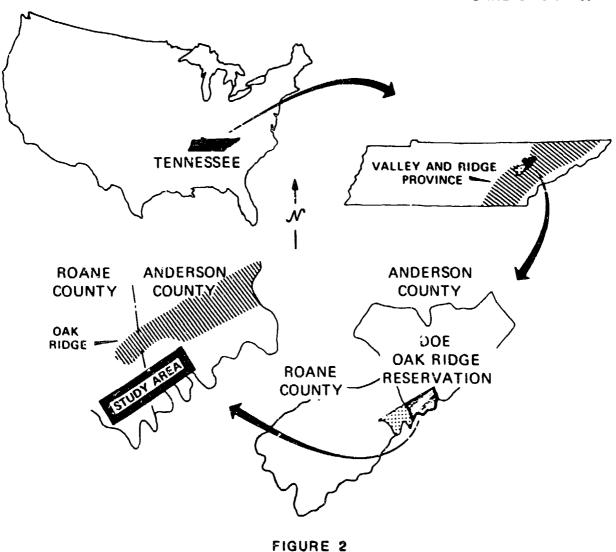


FIGURE 1



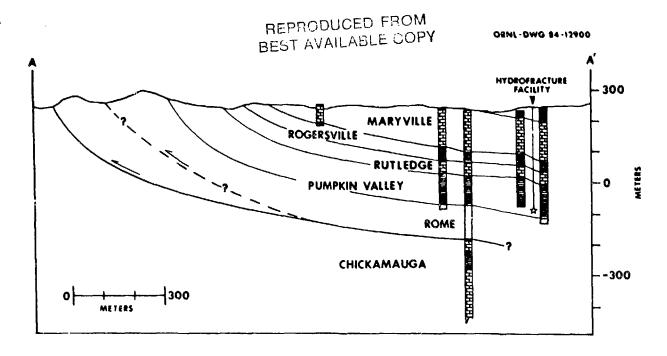


FIGURE 3

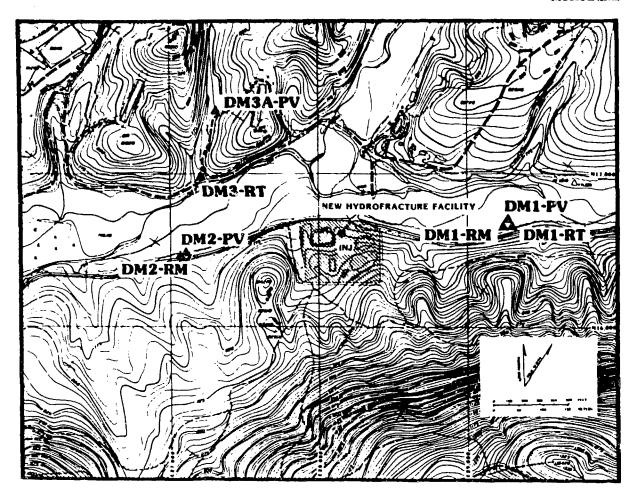


FIGURE 4

Table 1. Groundwater Monitoring Wells Surrounding the ORNL Hydrofracture Site

<u>Well</u>	Completion Formation	<u>Unit</u>	Distance (m/ft)1
DM1-PV DM2-PV DM3a-PV	Pumpkin Valley Shale Pumpkin Valley Shale Pumpkin Valley Shale	injection injection injection	300/1000 300/1000 300/1000
WOL No. 1 HF2 wells ² HF4 rock cover wells ⁴	Pumpkin Valley Shale lower Conasauga Group ³ Rogersville Shale/ Rutledge Limestone	injection upper confining/injection upper confining	1200/4000 900/3000 120/400 ⁵
DM1-RT DM3-RT DM1-RM DM2-RM	Rutledge Limestone Rutledge Limestone Rome Formation Rome Formation	upper confining upper confining lower confining lower confining	300/1000 300/1000 300/1000 300/1000

Distance from injection well at the fourth ORNL hydrofracture facility.

² Array of four core holes.

Wells are uncased core holes open to several formations.
 Array of eight cased wells surrounding the fourth hydrofracture facility.

⁵ Rock cover wells at the fourth hydrofracture site are located 60 to 120 m (200 to 400 ft) from the injection well.

Table 2. Chemical Analyses of Groundwaters at the ORNL Hydrofracture Facility¹

Sample No.	1*	2 ^b	3°	4d	5°	6 ^f	78
Depth (m)	320	324	320	266	182	213	330
Na+ K+ Mg+2 Ca+2 Sr+2 Ba+2 Fe _{tot} Mn _{tot} Cl- Br SO ₄ -2 NO ₃ -2 Alkalinity	59,000 240 4,100 22,000 2,300 680 170 140 150,000 1,400 <50 442	62,000 220 4,200 24,000 2,200 660 nm ³ nm ³ 156,000 1,800 <100 400	57,000 230 4,400 26,000 2,600 610 130 100 150,000 2,100 <50 1,991	12,000 77.0 260 2,800 210 1.5 23 3 24,000 210 522 <10 60	27,000 nm ³ 2,200 13,000 1,300 410 46 26 71,000 580 <50 20 <2	30,000 740 2,700 13,000 1,300 89 5.3 3.4 98,000 840 <50 18	37,000 330 1,300 11,000 1,400 8.6 3.1 1.1 91,000 750 <50 66 20
⁹⁰ Sr 3 ¹³⁷ Cs	3.5E4±2E3 nd ²	i.2E5±2.5E4 nd ²	9.4E4±2E3 nd ²	100±50 0.9±0.9	4.6±1.1 0.54±0.1	250±70 1.0±0.6	2.0E4±2E <1

¹ Chemical data are in μ g/mL. Radionuclide data are in Bq/L. Uncertainties for chemical data are approximately $\pm 10\%$, and for radionclides as stated.

² Not detected, ie. looked for but not found.

³ Not measured.

^a Well DM1-PV, sampled on January 31, 1986 (Haase, Switek, and Stow 1987).

b Well DM1-PV, sampled on November 19, 1986 (Haase, Switek, Stow, King, and Pollard 1987).

^c Well DM2-PV, sampled on January 31, 1986 (Haase, Switek, and Stow 1987).

d Well DM3a-PV, sampled on January 30, 1986 (Haase, Switek, and Stow 1987).

e Well HF4-S200RC, sampled on May 22, 1986 (Switek et al. 1987).

f Well DM1-RT, sampled on January 30, 1986 (Haase, Switek, and Stow 1987).

⁸ Well DM1-RM, sampled on January 30, 1986 (Haase, Switek, and Stow 1987).

DISCLAIMER

This repor, was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.